Metamaterials and photonic crystals – potential applications for self-organized eutectic micro- and nanostructures

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Recently in the field of photonics two new approaches for novel materials appeared. These materials are photonic crystals and metamaterials. In this paper the definition, methods of manufacturing and applications of these novel materials are discussed as well as the potentials of self-organized eutectic micro- and nanostructures for such optical applications. Examples of eutectic self-organized structures grown by the micro-pulling down method are presented.

Keywords*:* eutectic, photonic crystal, metamaterial, self-organized, micro-pulling down method, micro- and nanostructure.

PHOTONIC CRYSTALS

In recent years, two different types of materials are being developed in the area of photonics: photonic bandgap materials (photonic crystals) and metamaterials. Photonic crystals (PCs) are often called semiconductors for light. In a semiconductor there is a bandgap for electrons between the valence band and the conduction band. Electrons having energies in the bandgap are not allowed in the semiconductor crystal. The bandgap in a semiconductor arises from diffractional interaction of the electron wave function with the periodic atomic lattice, resulting in destructive interference for particular wavelengths. To observe diffraction of light a periodic lattice of artificial atoms is necessary with the lattice constant comparable with the light wavelength for which the bandgap is needed. That is why for visible wavelengths the lattice constant and the atoms should be in the range of few hundred nanometers. A net of such dielectric scatterers in a matrix of another dielectric can form a photonic crystal (PC), where the atoms are characterized by one index of refraction and the matrix by other index of refraction [1]. The field of photonic bandgap materials started to develop dynamically after two papers of S. John and E. Yablonovitch published both in the same volume of Phys. Rev. Lett. in 1987 [2,3]. It has been clear from these two papers that in such periodic materials with varying refractive index, spontaneous emission could be suppressed and light could be localized. There can be one-dimensional, two-dimensional and three-dimensional photonic crystals with a 1-dimensional photonic stopgap, 2-dimensional and 3-dimensional photonic bandgap, respectively. The one dimensional PCs are usually materials such as Bragg reflectors, interference filters which are manufactured by layer-by-layer deposition of materials with different refractive indexes. Two-dimensional ones can be in the shape of dielectric pillars embedded in another dielectric material (e.g. air) or air columnar holes embedded in dielectric material [4, 5]. Only the three-dimensional photonic crystals can have complete photonic bandgap (a direction and polarization independent). The first three-dimensional bandgap has been predicted theoretically in the structure of diamond: that is, a material with dielectric spheres placed in the atomic positions of diamond; or atomic positions of diamond connected by dielectric rods [6] The first three-dimensional PC has been obtained by Yablonovitch by drilling holes along 3 crystallographic axis of diamond in a material with high refractive index (now called Yablonovite) [6, 7]. The next structure which shows the complete photonic bandgap is a woodpile structure – originally invented by Sokoulis [8] and than miniaturized by Noda with an advanced wafer-fusion technique [9] to such dimensions that the bandgap was observed at the telecommunication wavelength - 1.5 µm. In this moment there are already many methods for manufacturing of photonic crystals: square spiral structure [10] was originally made by the glancing angle deposition method [11], and different 3-D structures can be created by holographic lithography, i.e. by interference of four non-coplanar laser beams in a film of photoresist [12]. It has also been found that natural opal forms a photonic structure. Natural opals consist of a regular three-dimensional crystalline array of colloidal silica spheres, several hundred nanometers in size [13]. Scientists started to follow nature forming synthetic opals by natural assembly of colloidal microspheres. The standard method for growing the initial opal is sedimentation of spheres from suspension. A synthetic opal can act as a template into which a semiconductor material can be infiltrated. Removing the template by annealing or etching leads to a tree-dimensional PC with periodic air-spheres embedded inside the material of high refractive index [14]. The other recently-applied method for generating PCs is direct laser writing (DLW), for which the spiral structures as well as woodpile and 'slanted pore' [15] structure manufacturing has been already demonstrated [16]. In order to make the PCs useful, defects have to be introduced into the lattice. Introducing defects to a PC is comparable to doping in a semiconductor. A point defect in PC acts as a microcavity [2, 3], which strongly traps and localize photons, a line defect like a waveguide in which photons can propagate [1,17], and a planar defect like a perfect mirror. Photons are Bose particles, and one defect can trap and control many photons (unlike electrons which are fermions). The ultimate goal of photonic crystal research is to obtain ultra-small optical and optoelectronic integrated circuits incorporating: nano-ampere laser arrays with different oscillation frequencies, waveguides that incorporate very sharp bends, optical modulators, wavelength selectors etc. Other applications include gas sensoring, antireflection coating for solar cells, PC lasers.

METAMATERIALS

An even more recent development in the field of photonics is metamaterials. "Metamaterials are engineered composites that exhibit superior properties that are not found in nature and not observed in the constituent materials" [18]. The difference between photonic crystals and metamaterials is that to have the photonic bandgap the atoms and the lattice constant in PCs have to be comparable in size with the wavelength, $a \approx \lambda$, because the effect of the bandgap arrises from diffraction. In the case of metamaterials artificial atoms (sub-units) and lattice constant have to be much smaller than the wavelength, $a << \lambda$, because diffraction should not appear. The wavelength passing through a metamaterial has to feel only the effective parameters of the material, such as effective magnetic permeability, μ, and effective electric permittivity, ε. From the electromagnetic point of view it is the wavelength which determines if a collection of atoms or sub-units is a material [19]. There can be metamaterials with different characteristics. The most famous in this moment are metamaterials with negative refractive index. The electromagnetic response of materials is mainly characterized by the index of refraction, n, where $n^2=\varepsilon\mu$. It has two components: electric permittivity, ε, and magnetic permeability, μ. While solving the equations for monochromatic waves Veselago [20] found that there appear to be only two available solutions for the refractive index: (i) when both ε and μ are positive then $n>0$; and (ii) when both are negative then $n<0$. Unlike a more conventional material with $n>0$, materials with $n<0$ bend rays of incident light to the same side (as the incident beam) of the normal. Naturally-occurring materials with $\varepsilon<0$ include noble metals like silver and gold. In these cases, the negative epsilon exist in the visible wavelengths. In order to obtain negative ε at longer wavelengths, a periodic structure composed of thin infinite wires arranged in a simple cubic lattice has been proposed [21, 22]. The magnetic response has been presented first for the split-ring structure. The combination of both gave a material with $n<0$ at microwave frequencies [23]. Recently, negative ε and μ were demonstrated in the visible region for a material made of nanorod pairs [24, 25]. Metamaterials with $n<0$ could find application, for example, as flat lenses. In conventional lenses with $n>0$ the resolution is limited by the wavelength. This is because only the far field is transmitted through a lens while the near field decays. In order to increase the resolution of an image the near field has to be transmitted and amplified. This is possible with a lens made of n<0 material. This is important for many areas of optics, eg. to increase the storage capacity of DVDs or to make smaller features in computer chips[26].

A different type of metamaterial is a material with giant dielectric constant. It has been shown that mixing a powder of $BaTiO_3$ with nanoparticles of nickel in an appropriate ratio to generate a percolated structure gives a very big dielectric constant [27]. At the percolation threshold the dielectric constant increases enormously. Another recently described phenomenon in the field is cloaking. It has been shown that, when an object is covered by a metamaterial made of special metal elements, the reflection (back scatter) and the shadow (forward scatter) are reduced by the metamaterial cloak [28].

EUTECTICS

There are many sophisticated techniques for manufacturing of photonic crystals and metamaterials. One of the ways could be also self-organization. The self-organized eutectic micro- and nanostructures has been identified as materials which could act as photonic crystals [29, 30] and also as metamaterials [31]. The eutectic is characterized by the formation of two un-mixable crystals from a completely mixable melt. There has been research going on metal-metal eutectics for many years, as materials with excellent mechanical properties. The oxide-oxide eutectics have been also investigated lately as materials with excellent flexural strength and creep resistance at high temperature [32]. Oxide-oxide eutectics have also been considered as materials with interesting optical properties [33, 34].Depending on different factors, such as the entropy of melting of both phases, volume fraction, growth rate and temperature gradient different forms of microstructure can be formed. They can be regular-lamellar, regular-rodlike, irregular, complex regular, quasi-regular, broken-lamellar, spiral and globular. The regular eutectic microstructures might find applications as photonic crystals: the lamellar ones as 1-D crystals, and rod-like as 2D crystals. From the point of view of metamaterials, other structures could be also interesting - for example the spiral geometry might suit as chiral metamaterial, or globular could find application in invisible materials [35] or in plasmon tunable materials (if the structure was metallodielectric) [36]. For metamaterials application hybrid eutectics might be important such as eutectics with one metallic phase (metallodielectric structures), a semiconducting phase, ferroelectric and ferromagnetic phases. A metallic or semiconducting phase should ensure the existence of plasma (a gas of free electrons in metals). The plasma frequency ω_p depends on the density of charges and their mass [37]. A negative ε is observed below the plasma frequency. In most metals, ω_p is in the ultraviolet region, which makes them a source of negative ε in the visible region. Doped semiconductors have ω_p in the infrared. In order to have the plasmon frequency at lower wavelengths the density of charges have to be diluted and the same the metal content have to be smaller. This has been shown already for a periodic structure made of thin metal wires [21, 22]. Ferroelectric and ferromagnetic phases could be also very interesting. Such materials are sources of polariton resonances. Having ferroelectric and ferromagnetic phases in the same eutectic (multiferroic eutectic) might create a n<0 material when both resonances (electric and magnetic) are in the same spectral region [38, 39].

Eutectics present the unusual characteristic of being at the same time a monolith and a multiphase material [40]. They have the potential for optical, electronic and magnetic applications [41]. They properties can be divided into two categories: additive properties and product properties. The additive properties depend on volume fraction and spatial distribution of the phases, while the product properties depend on interaction between the phases and depend on periodicity and the size of the phases [40, 41]. The additive properties can exist only in the eutectic, they can not exist in the singular phases. That is why the additive properties should be equal to the metamaterial properties.

There are different methods used for growth of eutectics: the Edge-Defined Film-Fed-Growth technique; the Bridgman method; the micro-pulling down method; and laser floating zone (LFZ). The micro-pulling down (m-PD) method in particular is well-suited for the directional growth of eutectics [42]. A fully-aligned eutectic structure can only be obtained when the crystal/melt interface is flat. The other necessary conditions are: steep temperature gradient, slow growth rate, and absence of convection [43, 44]. All these conditions can be realized in m-PD system.

THE MICRO-PULLING DOWN METHOD (M-PD)

The m-PD method was invented in Japan, originally for growth of single crystal fibres [45]. The growth of oxide-oxide eutectics for high strength materials has already been reported by this method [42]. The m-PD method utilises a crucible with a die at the bottom in which there is a centrally-placed nozzle. The raw materials are melted in the crucible; the melt passes through the nozzle, is touched with the seed crystal, and the crystal is then pulled down. Fig. 1 shows the scheme of the thermal system used in all the experiments reported here.

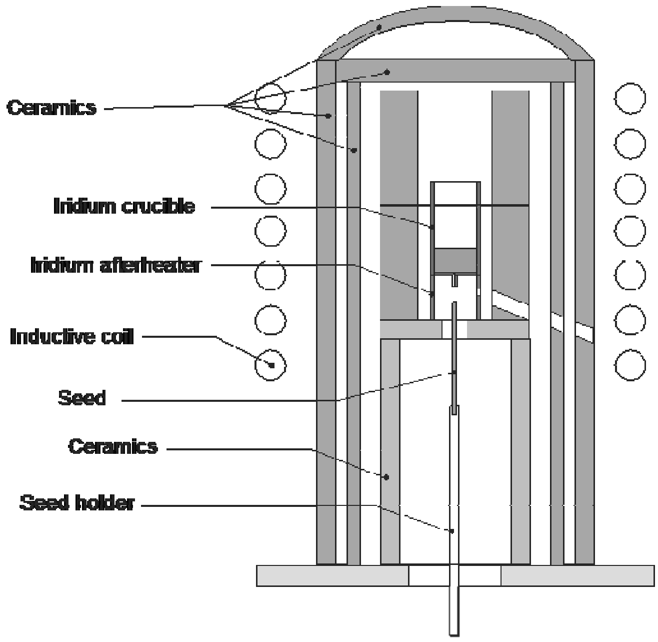

Fig. 1. Scheme of the thermal system used for all the experiment by the micro-pulling down method described in the paper [46].

SELF-ORGANIZED MICROSTRUCTURES OF EUTECTICS GROWN BY THE MICRO-PULLING DOWN METHOD

The rodlike microstructure (with potential application as a photonic crystal) has been observed, for example, in a $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ eutectic [29, 31, 46]. The size of the microstructure can be controlled by the pulling rate. Higher pulling rates give smaller sizes and smaller distances between the phases. In Fig. 2 the change of the microstructure dimensions is shown on the example of rodlike $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ eutectic.

For different eutectics at the same pulling rate, different dimensions of the microstructure can be obtained. For each eutectic there is valid a relation: λv^2=const, where v is growth rate, and λ

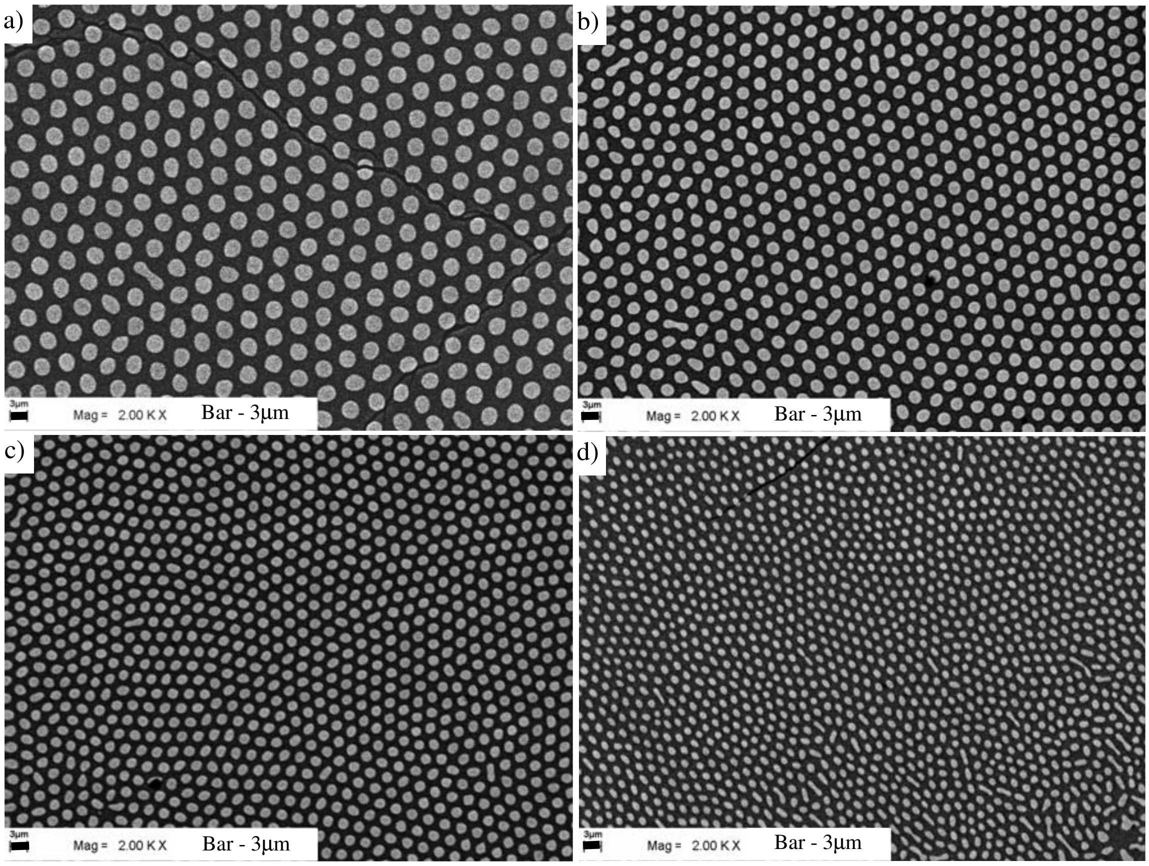

Fig. 2. The microstructure of $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ binary eutectic grown by the micro-pulling down method with differed pulling rates: a) 0.15 mm/min, b) 0.3 mm/min, c) 0.45 mm/min, d) 1 mm/min [29].

is lamellar spacing [43, 47]. In Fig. 3 the dependence of microrod mean diameter on the pulling rate is compared for two different eutectics with rodlike microstructure: $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ and $PrAlO_3$-$PrAl_{11}O_{18}$ in log-log representation (the line corresponds to d_2^2*(p.r.)=const.). Because of the character of this relationship, very high pulling rate would have to be applied to obtain really small precipitates of one phase in the matrix of the other phase. For example in the case of $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ eutectic the mean diameter decreases from 3.3 to 0.7 μm, grown at pulling rates 0.15 and 4 mm/min, respectively. And in the case of $PrAlO_3$-$PrAl_{11}O_{18}$ eutectic the mean diameter decreases from 1.87 to 0.39 μm, grown at pulling rates 0.15 and 5 mm/min, respectively. From Fig. 3 the constant of the λv^2=const. relation can be calculated. It is 36.6 μm^2mm/h for $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ eutectic and 97.7 μm^2mm/h for $PrAlO_3$-$PrAl_{11}O_{18}$ eutectic. For a fixed pulling rate, a smaller value of this constant suggests smaller distances between the phases. In comparison with other values presented in the literature for this constant e.g. between 27.4 and 1450 μm^2mm/h [30], the values given here are at the low end of the range. Recently, it has been shown that, at growth rates as high as 20 mm/min in the Al_2O_3-$Y_3Al_5O_{12}$-YSZ eutectic, whiskers of Al_2O_3 and of $Y_3Al_5O_{12}$ phases can be obtained with width *ca.* 100 nm, with smaller YSZ whiskers in between [48].

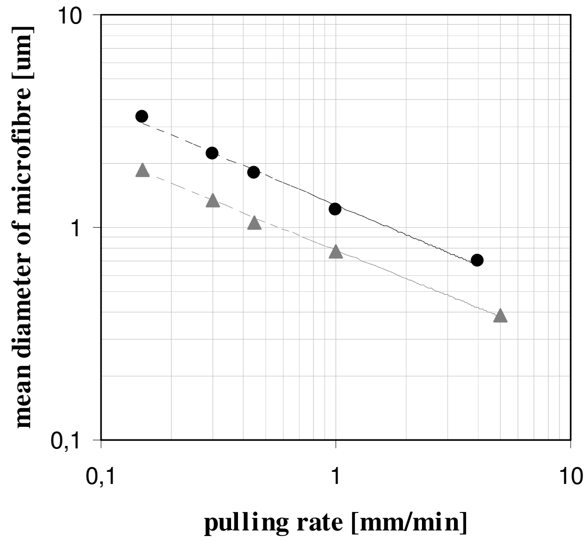

Fig. 3. Dependence of the microrods mean diameter (d_2) on the pulling rate for two different eutectics: $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ (•)[29] and $PrAlO_3$-$PrAl_{11}O_{18}$ (▲)[49] in log-log representation (the line corresponds to d_2^2(p.r.)=const.).*

The density of microrods can be as high as 3.1×10^6 microrods per square millimeter (this has been obtained in the case of $PrAlO_3$-$PrAl_{11}O_{18}$ eutectic with the microrod mean diameter of 0.39 μm [49]). The periodicity of the eutectic microstructure can be investigated by the linear covariance function [50] as well as by the radial distribution function (RDF) [51]. In both cases, if these functions show periodicity it implies that the investigated structure is also periodic. Both eutectics, $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ and $PrAlO_3$-$PrAl_{11}O_{18}$, were characterized with these functions, showing high periodicity for all the pulling rates [31, 49]. In Fig. 4 the linear covariance function is shown for the $PrAlO_3$-$PrAl_{11}O_{18}$ eutectic grown with the 0.15 mm/min pulling rate [49]. In the investigated eutectics the matrix phase grew in one crystallographic direction [29, 52], while the pattern forming phase did not show a distinguished direction in the whole investigated rod of the eutectic; but the adjacent microrods investigated by electron back scatter diffraction showed the same crystallographic direction [46].

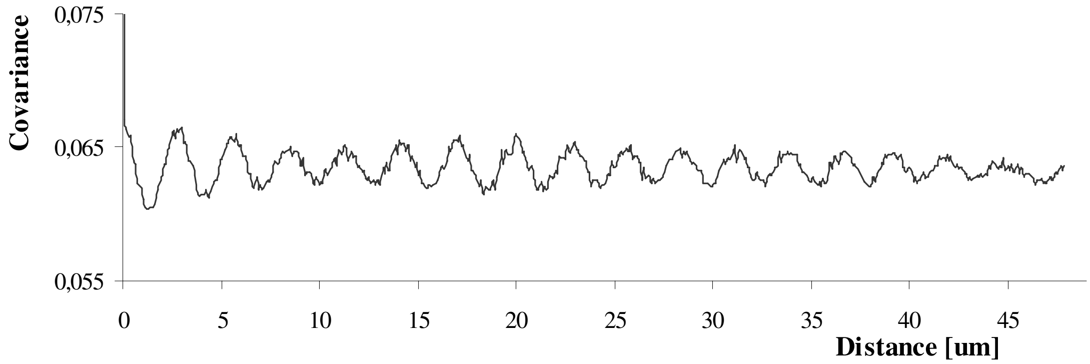

Fig. 4. The covariance function determined along the horizontal direction - C(x), for the sample of $PrAlO_3$-$PrAl_{11}O_{18}$ eutectic grown with the pulling rate 0.15 mm/min [49].

Other examples of the microstructure geometries obtained for eutectics grown by the micro-pulling down method are presented in Fig. 5.

Eutectics with one metallic phase can be obtained in different ways. The first method is to grow such eutectics from the melt [53], although very little work has been done in this field so far. The other way is to grow an eutectic with a metal oxide phase which can be reduced, which for example has been done in the case of following eutectics: $NiO/ZrO_2(CaO)$ [54] or NiO-YSZ and CoO-YSZ eutectics [55]. After annealing in a reducing atmosphere, porous cermets with metallic particles of nickel or cobalt were obtained. The other method to obtain dielectric-metal structures from eutectics is to remove one of the two phases by etching and to then fill the empty space with metal. Example of such structures have been created on the base of $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ eutectic. Depending on the composition of the eutectic rod it was possible to etch away either the matrix phase ($Tb_3Sc_2Al_3O_{12}$) or the microrod phase ($TbScO_3$), Fig. 6a,b [29, 31]. The metallodielectric structure/surface has been obtained by evaporating the metal on the etched surface of eutectic, Fig. 6c,d.

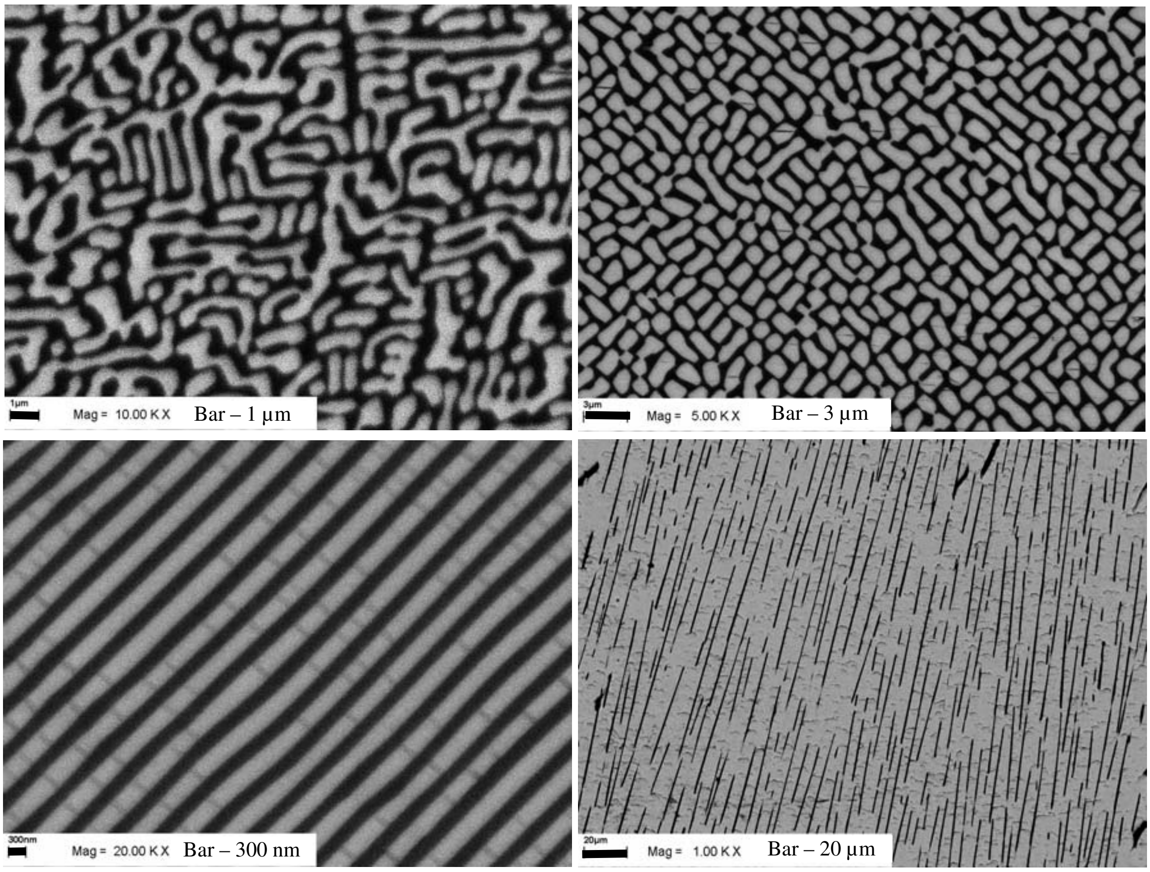

Fig. 5. The microstructure of binary eutectics grown by the micro-pulling down method: a) percolated-like microstructure of $PrAlO_3$-Pr_2O_3 eutectic (cross-section, p.r.=5 mm/min) [52], b) brick-like microstructure of $PrAlO_3$-Pr_2O_3 eutectic (cross-section, p.r.=0.45 mm/min), c) lamellar microstructure observed in $PrAlO_3$-Pr_2O_3 eutectic (cross-section, p.r.=5 mm/min), d) broken-lamellar microstructure of ZnO-$ZnWO_4$ eutectic (cross-section, p.r.=0.05 mm/min)[56].

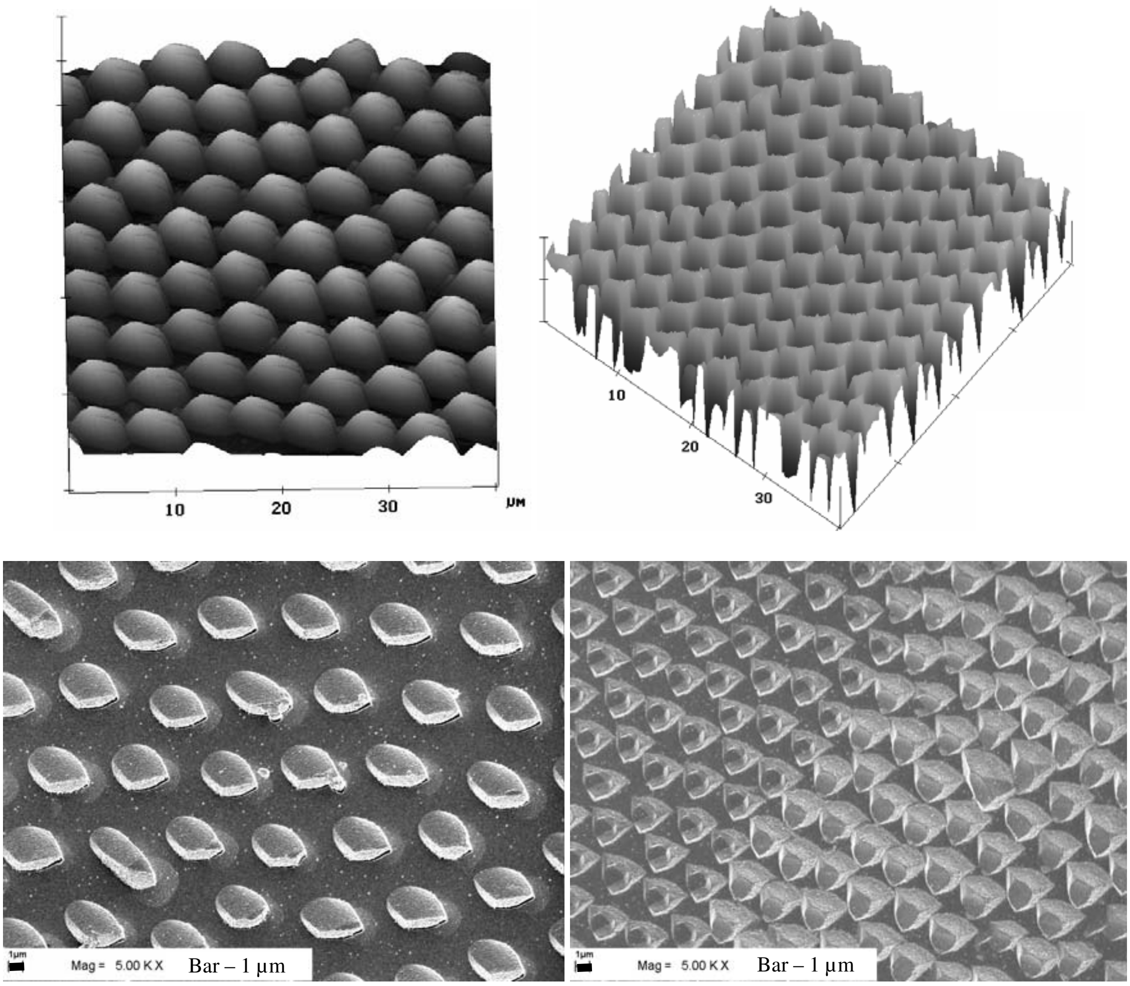

Fig. 6. Surface structuring obtained after etching of $Tb_3Sc_2Al_3O_{12}$-$TbScO_3$ eutectic: a) $TbScO_3$ microrods embedded in air (AFM image), b) air-holes embedded in $Tb_3Sc_2Al_3O_{12}$ matrix (AFM image), c) metal-dielectric surface obtained after depositing metal on the structure shown in (a) (SEM image), d) metal-dielectric surface obtained after depositing metal on the structure shown in (b) (SEM image) [29].

CONCLUSIONS

Self-organized eutectic structures may find its place in the field of photonics, showing different optical properties. Regular (lamellar, rodlike) structures of eutectics suit to photonic crystal requirements, though the photonic bandgap effect has still to be proven. The product properties of eutectics make them ideal candidates for metamaterials with different functionalities. Eutectics with such phases as metallic, semiconducting, ferroelectric and ferromagnetic appear to represent the most interesting directions for further research on metamaterials.

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